

## Effect of Butadiene End-Capping of Arms in a Star Polystyrene on Solution Properties, Bulk Dynamics, and Bulk Thermodynamic Interactions in Binary Blends

Jae S. Lee, Roderic P. Quirk, and Mark D. Foster\*

Maurice Morton Institute of Polymer Science,  
The University of Akron, Akron, Ohio 44325-3909

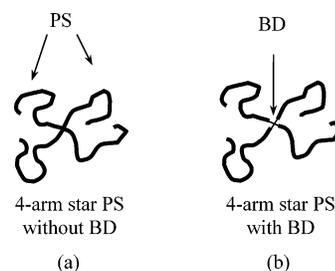
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### Introduction

An important route to well-defined star polymers for incisive study of the changes in properties with molecular architecture is anionic polymerization.<sup>1,2</sup> Star-branched polystyrenes have been particularly widely studied because comparison can be readily made to linear polystyrenes that have been very extensively investigated.<sup>3–7</sup> In general, well-defined star polystyrenes with high functionality cannot be synthesized without using a linking agent containing a spacer group or by end-capping the arm precursor poly(styryl)lithium with a few units of a monomer such as isoprene or butadiene (BD) that forms a less sterically hindered organolithium chain end. If end-capping is not done, steric hindrance between the linking agent and the poly(styryl)lithium arm precursor generally leads, for practical reaction times, to incomplete linking and the formation of a mixture of stars having various functionalities.<sup>1,8</sup> Studies of the properties of star polystyrenes or their blends have sometimes assumed that the presence of the end-capping units does not appreciably affect the properties of the star-branched polymer.<sup>5,6,9,10</sup> Roovers and Toporowski<sup>11</sup> reported that end-capping with isoprene lowered the  $T_g$  of a polystyrene star polymer. However, we are unaware of any systematic study of the effect of end-capping on star hydrodynamic size or thermodynamic behavior. In this contribution we probe the differences in intrinsic viscosity, glass transition temperature, and thermodynamic behavior of two well-defined, anionically polymerized 4-arm star polystyrene analogues, one with 1 or 2 BD units on each arm and one without the butadiene units (see Figure 1). Four is the highest number of arms for which a well-defined polystyrene (PS) star having the target functionality can be made without end-capping.

Of particular interest is the question of whether the end-capping of the star arms by a few units of BD appreciably alters the thermodynamics of a blend of star-branched and linear polystyrenes. Blends of chains that differ only in molecular architecture have promise for applications in which one desires to tailor rheological behavior while maintaining the advantages of a certain repeat unit chemistry. It has been predicted theoretically<sup>12</sup> and demonstrated experimentally<sup>5,6,9</sup> that when star polymers are blended with linear polymers of the same repeat chemistry, the comparatively subtle difference in the architectures of the two chains results in a measurable thermodynamic exchange interaction in the bulk.<sup>5,6</sup> In particular, it has been shown<sup>5,6</sup> that the



**Figure 1.** Schematic illustration highlighting the difference between the 4-arm polystyrene without butadiene units (a) and with butadiene units (b).

interaction parameter due to the architectural differences increases monotonically with star functionality (number of arms per star). The presence of spacer groups or end-capping units could result in an enthalpic contribution to the interaction parameter and changes in other physical properties that should not be attributed to the architecture per se. In this work we demonstrate that while end-capping alters the intrinsic viscosity of a 4-arm star PS and has a profound impact on the glass transition temperature, it does not change the thermodynamic behavior of a star/linear blend appreciably.

### Experimental Section

**Synthesis and Characterization.** Styrene, benzene, and butadiene were purified as described previously.<sup>13</sup> 1,2-Bis(dichloromethylsilyl)ethane (DMSE) (Aldrich, 98%) was purified by distillation at 120 °C on the vacuum line. The first third of the distillate was discarded; the next third was collected, diluted with purified benzene in a drybox, ampulized, and heat-sealed on the vacuum line. The poly(styryl)lithium arm precursors ( $M_n = 4100$  g/mol) were synthesized in benzene using *sec*-butyllithium as initiator, all glass reactors, and standard high-vacuum techniques.<sup>14</sup> Half of each poly(styryl)lithium precursor (PSLi) was linked with 1,2-bis(dichloromethylsilyl)ethane ( $[\text{Si}-\text{Cl}]/[\text{PSLi}] = 0.8$ ) to make a 4-arm star polymer without butadiene (BD) end-capping units. The remainder of the living poly(styryl)lithium was end-capped using 2 equiv of BD to form PS-*b*-PBBDLi; the crossover reaction was monitored using UV-vis spectroscopy (Hewlett-Packard 8452A diode array spectrophotometer). Aliquots of PSLi and PSLi-*b*-PBBDLi were terminated with methanol and characterized with size exclusion chromatography (SEC) (Viscotek model 301 triple detector system with a Waters140R differential refractometer and DAWN-EOS laser light scattering detector), <sup>1</sup>H NMR (Varian 300 MHz spectrometer), and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (Bruker Daltonics Reflex III) to determine the number of BD units on the arms. The remaining PS-*b*-BDLi was linked with 1,2-bis(dichloromethylsilyl)ethane ( $[\text{Si}-\text{Cl}]/[\text{PS-}b\text{-BDLi}] = 0.8$ ). The linking reactions proceeded for 1 week for PSLi linking (4PS) and for 2 days for PS-*b*-PBBDLi linking (4PSwBD), followed by quenching with degassed methanol. Star polymers were isolated by precipitation into degassed methanol. Each 4-arm star polymer was separated from the excess of corresponding arm polymer using toluene as good solvent and methanol as poor solvent. A deuterated linear analogue (dPS) was synthesized by *sec*-butyllithium-initiated polymerization of purified *d*<sub>8</sub>-styrene (Polymer Source, Inc.). After fractionation, the molecular weights, the intrinsic viscosities, and the glass transition temperatures ( $T_g$ ) of the three polystyrenes were measured using SEC, capillary viscometry (Cannon-Ubbelohde), and differential scanning calorimetry (DSC) (TA Instruments DSC

\* Corresponding author: Tel 330-972- 5323, Fax 330-972-5290; e-mail mfoster@uakron.edu.

Table 1. Molecular Characterization of the Polystyrenes

samples	no. of BD units per arm <sup>a</sup>	$M_{n(\text{arm})}^b$ (g/mol)	$M_{n(\text{star})}^b$ (g/mol)	$f^c$	$[\eta]_{\text{star}}^d$ (dL/g)	$[\eta]_{\text{linear}}$ (dL/g)	$g'^g$
4-arm star PS without end-capping	0	4100	16 700	4.0	$0.076 \pm 0.002$	$0.105 \pm 0.003^e$	$0.72 \pm 0.03$
4-arm star PS with end-capping	1.4	4200	17 200	4.0	$0.085 \pm 0.005$	$0.112 \pm 0.003^f$	$0.76 \pm 0.05$
linear d-PS			16 700			$0.110 \pm 0.003$	

<sup>a</sup> Average of results from MALDI-TOF ( $\pm 1\%$ ) and <sup>1</sup>H NMR ( $\pm 2\%$ ). <sup>b</sup> SEC-RI measurement coupled with light scattering ( $\pm 5\%$ ). <sup>c</sup> The degree of branching:  $f = M_{n(\text{star})}/M_{n(\text{arm})}$ . <sup>d</sup> Determined in toluene at 35 °C. <sup>e</sup> Interpolated from a linear fit to intrinsic viscosities of PSs with molecular weights of 14 500, 18 900, and 20 800 g/mol. <sup>f</sup> Calculated as described in the text using eq 1. <sup>g</sup> Branching factor:  $g' = [\eta]_{\text{star}}/[\eta]_{\text{linear}}$ .

Table 2. Molecular Weights and Glass Transition Temperatures of Various PSs

samples	$M_{n(\text{arm})}$ (g/mol)	$M_{n(\text{star})}^a$ (g/mol)	$M_w/M_n$	$T_g^b$ (°C)
4-arm star PS without end-capping	4100	16700	1.01	85
4-arm star PS with end-capping	4200	17200	1.01	76
linear d-PS		16700	1.01	99
linear h-PS		15000	1.02	98
linear h-PS <sup>c</sup>		9000	1.02	96
linear h-PS <sup>c</sup>		7100	1.02	87
arm PS without end-capping		4100	1.04	81
arm PS with end-capping		4200	1.04	76

<sup>a</sup> SEC-RI measurement coupled with light scattering ( $\pm 5\%$ ).

<sup>b</sup> Measured at a heating rate of 10 °C/min using DSC ( $\pm 1$  °C).

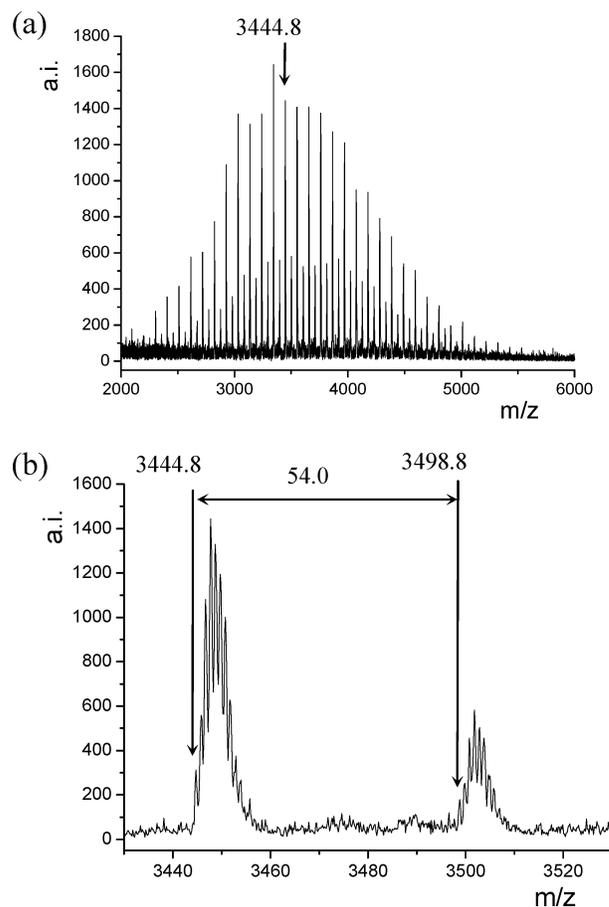
<sup>c</sup> Purchased from Polymer Laboratories, Ltd.

2910, 10 °C/min), respectively. The results are summarized in Table 1. Values of  $T_g$  for the stars, arm precursors, and deuterated linear analogues to the two stars are presented in Table 2 along with values for three linear hydrogenous PS samples. One is a near analogue for the stars ( $M_n = 15\,000$  g/mol) that was synthesized by *sec*-butyllithium-initiated polymerization of purified styrene. The other two ( $M_n = 7100$  and 9000 g/mol) are standards purchased from Polymer Laboratories, Ltd.

**SANS Measurement.** Sample blends containing 50 vol % star and 50 vol % dPS were prepared by dissolving the polymers in toluene and then solution casting in Teflon beakers (Aldrich). Films dried under a roughing vacuum (30 in.Hg) at 70 °C for 5 days were pressed (3 tons, 120 °C, 3 min) inside 1 mm thick brass rings and then loaded into standard sample cells.<sup>15</sup> SANS experiments were carried out on the NG3 30 m SANS instrument at the National Institute of Standards and Technology using a wavelength of 6 Å ( $\Delta\lambda/\lambda = 0.15$ ). Scattering intensities were measured at temperatures of 120, 140, 160, 180, and 200 °C at two different sample-to-detector distances (13 and 4.5 m), providing a range of scattering vector,  $q$ , of  $0.004 \text{ \AA}^{-1} \leq q \leq 0.14 \text{ \AA}^{-1}$ . The scattering data were corrected for background, empty cell scattering, detector sensitivity, and incoherent scattering as estimated from measurements of 100% hydrogenous PS and 100% deuterated linear analogue samples.

## Results and Discussion

**Characterization of Arm Polystyrenes and 4-Arm Star Polystyrenes.** That the end-capping reaction indeed proceeded to completion was indicated by a shift in the UV-vis absorbance spectrum maximum (not shown) from 335 nm (PSLi) to 295 nm (PS-*b*-PBDLi). In the MALDI-TOF mass spectrum of the polymer formed after the crossover reaction, shown in Figure 2, pairs of peaks separated by 54.0 Da appear, confirming the incorporation of the butadiene units. The first big peak in Figure 2b was assigned to arm precursors containing 32 units of styrene and one unit of BD [i.e.,  $\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{32}-\text{C}_4\text{H}_7\cdot\text{Ag}^+$ , calcd monoisotopic mass 3444.9 Da,  $m/z$  observed = 3444.8], and the smaller peak at higher mass was assigned to arm precursors also having 32 polystyrene units, but having two units of BD [i.e.,  $\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{32}-\text{C}_8\text{H}_{13}\cdot\text{Ag}^+$ , calcd monoisotopic mass 3499.0 Da,  $m/z$  observed = 3498.8]. Furthermore, there is no peak corresponding to arm precursor containing 33 units of styrene with no BD units [i.e.,  $\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{33}-\text{H}\cdot\text{Ag}^+$ , calcd monoisotopic mass 3495.0 Da, not observed] between the two peaks. This means that each and every polystyryllithium arm precursor has attached to it exactly one or two butadiene units. There are none with zero or three units of BD. The average number of BD units per arm estimated from the relative intensities of the two peaks was 1.4. This estimate of the number of BD units was corroborated using <sup>1</sup>H NMR. After the crossover reaction, new peaks appeared in the region  $\delta$  4.8–5.6 ppm assignable to the protons on the double



**Figure 2.** MALDI-TOF mass spectrum of the polystyrene-*b*-oligo(butadiene) arm precursor: (a) entire spectrum, (b) enlargement resolving one pair of peaks corresponding to polystyrenes with 32 styrene units and one (left major peak) or two (right major peak) BD units.

Da,  $m/z$  observed = 3444.8], and the smaller peak at higher mass was assigned to arm precursors also having 32 polystyrene units, but having two units of BD [i.e.,  $\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{32}-\text{C}_8\text{H}_{13}\cdot\text{Ag}^+$ , calcd monoisotopic mass 3499.0 Da,  $m/z$  observed = 3498.8]. Furthermore, there is no peak corresponding to arm precursor containing 33 units of styrene with no BD units [i.e.,  $\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{33}-\text{H}\cdot\text{Ag}^+$ , calcd monoisotopic mass 3495.0 Da, not observed] between the two peaks. This means that each and every polystyryllithium arm precursor has attached to it exactly one or two butadiene units. There are none with zero or three units of BD. The average number of BD units per arm estimated from the relative intensities of the two peaks was 1.4. This estimate of the number of BD units was corroborated using <sup>1</sup>H NMR. After the crossover reaction, new peaks appeared in the region  $\delta$  4.8–5.6 ppm assignable to the protons on the double

bonds of the BD units. This region included peaks for the protons from  $-\text{CH}=\text{CH}-$  units in the oligomeric butadiene chain having *cis*-1,4- and *trans*-1,4-microstructure as well as peaks for protons from vinyl groups ( $\text{CH}_2=\text{CH}-$ ) in the units with 1,2-microstructure. The vinylidene protons from the  $\text{CH}_2=$  groups in the 1,2-microstructure are assigned to the resonances in the  $\delta$  4.8–5.01 ppm region, and the protons from the  $-\text{CH}=\text{CH}-$  groups in the units with *cis*-1,4-, *trans*-1,4-, and 1,2-microstructure are assigned to peaks in the  $\delta$  5.03–5.6 ppm region. In the spectrum the peak assignable to the  $\text{CH}_2=$  protons in 1,2-microstructural units was not separated clearly from the peak for the  $-\text{CH}=\text{CH}-$  protons in the *cis*-1,4-, *trans*-1,4-, and 1,2-microstructural units due to the presence of a styrene unit next to butadiene. Allowing for the overlap of the peaks, the best estimate of the amount of 1,2-microstructure was 2–5 mol %. Thus, the number of BD units added to the arms was estimated from the ratio of the area for peaks corresponding to the  $-\text{CH}=\text{CH}-$  and  $\text{CH}_2=\text{CH}-$  moieties in BD (2H;  $\delta$  4.8–5.6 ppm) to the area for the methyl part of *sec*-Bu (6H;  $\delta$  0.45–0.8 ppm) or the phenyl ring part of styrene (5H;  $\delta$  6.2–7.3 ppm); the observed area ratios were 0.33 and 0.016, respectively. The average of these two NMR determinations of the butadiene units per molecule is 1.4. Thus, the poly(styryl)lithium was completely end-capped with BD, and the average number of BD units per molecule was 1.4, a value substantiated by both techniques, MALDI-TOF and NMR. The number-average molecular weight of arms before end-capping measured by SEC was  $4100 \pm 200$  g/mol, and that of arms after end-capping was  $4200 \pm 200$  g/mol. Thus, the use of the same precursor arm polystyrenes, with and without a small amount of BD, for both stars ensured that the molecular weights of the two stars were as close as synthetically practical.

**Comparison of Solution and Bulk Dynamic Properties.** Differences in both the intrinsic viscosity and the bulk dynamic properties of the two stars, shown in Table 1 and Table 2, give evidence of the presence of the BD units in 4PSwBD. First, the intrinsic viscosity of 4PSwBD is larger than that of 4PS. This difference can be explained simply by calculating the difference in molecular friction to be expected from the addition of the BD units. The intrinsic viscosity, in toluene at 35 °C, of linear PS homopolymer having the same molecular weight as that of 4PS was interpolated from measured values of the intrinsic viscosities of linear polystyrene standards having molecular weights of 14 500, 18 900, and 20 800 g/mol (as determined using the same protocol as for all other polymers). The intrinsic viscosity for PB<sup>16</sup> was calculated using an empirical equation as  $[\eta]_{\text{PB}} = 2.85 \times 10^{-2} M_n^{0.73}$ , which is appropriate for values of  $M_n$  from  $0.11 \times 10^5$  to  $400 \times 10^5$  g/mol. The change of the intrinsic viscosity of a linear PS chain due solely to the incorporation of the short BD block can be predicted using an empirical relationship for linear random copolymers:<sup>17</sup>

$$[\eta]_{\text{copol}} = (w_{\text{PS}}[\eta]_{\text{PS}}^{2/3} + w_{\text{PB}}[\eta]_{\text{PB}}^{2/3})^{3/2} \quad (1)$$

where  $[\eta]_{\text{PS}}$  and  $[\eta]_{\text{PB}}$  are the intrinsic viscosities of the PS and polybutadiene (PB) homopolymers with the same molecular weight and architecture as the copolymer. In this case the weight fraction  $w_{\text{PB}}$  is 0.018. The measured intrinsic viscosity of a linear PS homopolymer of the same molecular weight as the star is 0.105 dL/g,

while the viscosity expected for a linear random copolymer of BD content comparable to that of 4PSwBD is 0.112 dL/g, an increase of 0.007 dL/g. The measured increase in  $[\eta]$  for the star with the addition of the BD is 0.009 dL/g, suggesting that the entire increase can be explained by the greater friction of the BD units. The  $g'$  value ( $g' = [\eta]_{\text{star}}/[\eta]_{\text{linear}}$ ) of a 4-arm star polymer in good solvent expected from the model of Stockmayer and Fixman<sup>18</sup> is 0.71. Comparison with this value is complicated in the present case by two facts. First, the chains lie in a regime of molecular weight for which the behavior of linear chains in toluene is drifting from that characteristic of good solvent (exponent of 0.74) to that characteristic of  $\Theta$  solvent (0.5) as molecular weight decreases.<sup>19</sup> Second, for comparatively short arms, the theta temperature of a four-arm PS star (without end-capping) in cyclohexane has been shown to be<sup>19</sup> depressed relative to that of a linear chain in cyclohexane, and thus toluene is a slightly better solvent for 16K star chains at 35 °C than for 16K linear chains. Thus, one might expect the measured values of  $g'$  to lie between that expected for good solvent and that expected for a  $\Theta$  solvent, and to within the experimental uncertainties this appears to be the case for both types of star. In fact, the values of  $g'$  for the two stars do not differ by an amount that is experimentally significant.

The glass transition temperatures of the two stars differ significantly (see Table 2), and this difference proved to be very interesting. The  $T_g$  of 4PS (85 °C) is 14 °C lower than that of a hydrogenous linear analogue (see Table 2). A simple free volume argument contending that each molecular end contributes excess free volume<sup>20</sup> leads one to expect the value of  $T_g$  for 4PS to be equal to that for a linear chain of molecular weight comparable to the span of the star.  $T_g$ 's for linear PS standards with molecular weights of 7100 and 9000 g/mol are given in Table 2, and from that data a value of  $T_g$  for a linear chain of molecular weight 8200 g/mol may be interpolated to be 92 °C. The value of  $T_g$  measured for 4PS (85 °C) is 7 deg lower than this. We conjecture that this is due to the fact that the span of the star has a butyl initiator fragment at each of its two ends, while the linear chain analogue has a butyl fragment at only one end and is terminated by a proton at the other. The butyl fragments are much more flexible than the polystyrene backbone. In any case, of greater interest is the fact that the  $T_g$  of 4PSwBD (76 °C) is an additional 9 °C lower than that of 4PS due to the incorporation of the flexible BD units. This is about double the effect reported for end-capping with isoprene.<sup>11</sup> The  $T_g$  of 4PSwBD is close to the theoretical value (78 °C) predicted using the Fox equation<sup>21</sup>

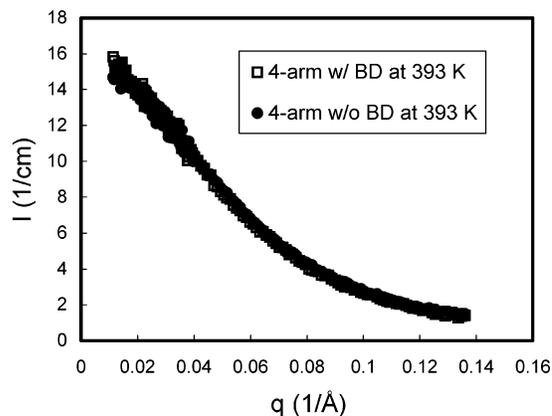
$$\frac{1}{T_g} = \frac{W_{\text{PS}}}{T_{g,\text{PS}}} + \frac{W_{\text{PB}}}{T_{g,\text{PB}}} \quad (2)$$

for a corresponding copolymer of styrene and BD ( $W_{\text{PB}} = 0.018$ ,  $W_{\text{PS}} = 0.922$ ,  $T_{g,\text{PB}} = -94$  °C<sup>22</sup>) when  $T_{g,\text{PS}}$  is taken to be that of the star without end-capping (85 °C). Thus, one possible explanation of the  $T_g$  for 4PSwBD is simply that it is a result of a copolymer effect. However, consideration of the  $T_g$  values of the two arm precursors themselves (Table 2) suggests another explanation. The  $T_g$  for the arm without end-capping, 81 °C, is distinctly lower than that of the star 4PS, 85 °C. In contrast, the  $T_g$  for the arm with end-capping, 76 °C, is the same as that of the star 4PSwBD. The dynamics of the star with

end-capped arms is like that of the arms themselves, suggesting that the inclusion of even one or two flexible BD units may dynamically decouple the arms from the core. We conjecture that this is due to particularly fast, local dynamics in butadiene units that can be active even in highly constrained environments. A hopping motion in PBD melts that has been seen experimentally by multiple groups<sup>23–25</sup> and seen in simulations by Kim and Mattice<sup>26</sup> could perhaps be the basis of the end-capping unit's high mobility. However, in the present case a single BD unit is, or at most two BD units are, located between the star core and the polystyrene arm. At temperatures in the neighborhood of the measured  $T_g$ , the polystyrene is quite rigid. Thus, more pertinent to the present discussion is another fast motion, identified by Dodge and Mattice,<sup>27</sup> that is possible in poly-(1,4-*trans*-butadiene) even in a highly constrained environment. They explained with molecular dynamics simulations<sup>27</sup> the experimental observations of Sozzani et al.<sup>28</sup> that when an *all-trans*-PBD chain is confined in the channel of an inclusion complex, it is still sufficiently mobile so that the C–<sup>2</sup>H bond is completely averaged about the axis of the channel during the lifetime of an NMR experiment. Dodge and Mattice argue that this is due to coupled conformational transitions that can occur across the double bond of a BD unit. These transitions will be active in the constrained environment represented by the stars with end-capped arms, even though only one or two BD units are located on each arm. The time scale of these motions is at least a factor of  $10^{10}$  smaller than that for the polystyrene segmental motion near the star  $T_g$ .

We anticipate that measurements with higher molecular weight stars would show that the incorporation of the BD units no longer measurably perturbs the value of  $T_g$  of the star for molecular weights above an arm molecular weight of 40 000 g/mol. The  $T_g$  of linear PS becomes nearly independent of molecular weight for molecular weights above that value.<sup>20</sup> We may also conjecture on how incorporating BD units might affect the behavior of stars of higher functionality. If the arms are indeed dynamically decoupled from the core by fast dynamics that are active even in constrained environments, then the  $T_g$  of a star with end-capping should not change with the number of arms if the arm length and exact number of BD units per arm is kept constant. If the arms are not fully dynamically decoupled or if the BD fast dynamics are hindered by having additional crowding at the core, the  $T_g$  could increase with star functionality. How the  $T_g$  values of stars without end-capping would compare to those of stars with end-capping cannot be tested experimentally because there currently exist no synthetic means of creating high-functionality analogues of star PS with and without end-capping.

**Comparison of Bulk Thermodynamic Interactions.** Small-angle neutron scattering (SANS) data from 50/50 blends of 4PS with dPS and 4PSwBD with d-PS measured at 120 °C are presented in Figure 3. The scattering intensity from the two blends is the same within experimental uncertainty. This observation by itself answers the question of whether the use of end-capping of star arms by a few units of BD appreciably alters the thermodynamics of a star/linear blend. It does not in the case of the 4-arm star, even when this end-capping has significantly impacted the dynamics of the star. Since the actual value of the bulk interaction



**Figure 3.** SANS absolute intensities as a function of scattering vector for 50/50 (vol %/vol %) binary blends of 4PS with dPS and 4PSwBD with dPS. The two curves are the same within experimental uncertainty.

parameter in such blends is of continuing interest to us, we also have extracted the value of the exchange interaction parameter,  $\chi$ , from the data assuming a structure factor derived for a regular branched  $n$ -arm star in the incompressible random phase approximation.<sup>29</sup> Strictly speaking, both 4PS and 4PSwBD are copolymers. Both stars have, in addition to non-styrenic chemistry at their cores, *sec*-butyl fragments at the ends of all the arms. Since the details of this chain end chemistry are identical for the two stars, we neglect these details in the extraction of the value of an effective  $\chi$ . We treat each star polymer as a homopolymer, arguing that the data set considered here does not contain sufficient information to make fitting of the data by including an additional interaction parameter between the arm ends and the arm interior segments a useful exercise. In this approximation, in which the chain ends are not differentiated, the measured intensity for the binary blend of the star polymer 4PS (component 1) and the linear polymer (component 2) is given as<sup>29</sup>

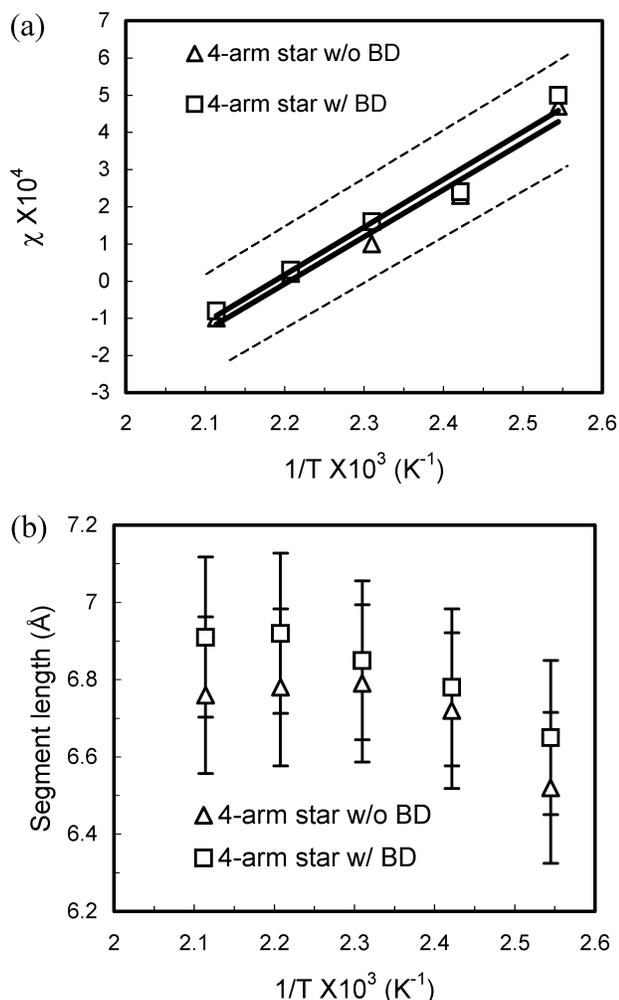
$$\frac{\left[\left(\frac{b}{V}\right)_1 - \left(\frac{b}{V}\right)_2\right]^2}{[I(q)]_{\text{measured}}} = \frac{1}{\phi_1 N_1 S_1(R_{g,1}, q)} + \frac{1}{\phi_2 N_2 S_2(R_{g,2}, q)} - \frac{2\chi}{V_0} \quad (3)$$

where  $V_1$  is the segment molar volume (chosen as  $V_2 = V_1 = 100 \text{ cm}^3/\text{mol}$ ),  $\phi_i$  is the volume fraction of species  $i$ ,  $N_i$  is the number of segments per chain, and  $(b/V)_i$  is the scattering length density for component  $i$ . The structure factors for the star and linear polymers given by Benoit are<sup>30</sup>

$$S_{\text{star}} = \frac{2}{f x^2} \left( x - 1 + e^{-x} + \frac{f-1}{2} (1 - e^{-x})^2 \right) \quad (4)$$

$$S_{\text{linear}} = \frac{2}{x^2} (x - 1 + e^{-x}) \quad (5)$$

where  $x = (qa)^2/6$  and  $a$  is the statistical segment length. The values of both  $a$  and  $\chi$  were allowed to vary in fitting the curves. The resulting estimates of  $a$  and  $\chi$  for all temperatures measured are presented in Figure 4. The value of  $\chi$  at 120 °C for 4PS is  $4.7 \times 10^{-4}$ . This is a factor of 3.6 higher than the value of  $\chi$  ( $1.3 \times 10^{-4}$ ) reported



**Figure 4.** Variation in (a) the effective interaction parameter,  $\chi$ , and (b) segment length,  $a$ , with temperature for the two star/linear blends.

by Greenberg et al.<sup>5,6</sup> for an isotopic blend of 18 wt % 4-arm PS star (not end-capped, 85K) in linear dPS (143K). The theory of Fredrickson et al.<sup>12</sup> anticipates that the magnitude of the contribution to  $\chi$  attributable to entropic effects should vary as

$$\chi_e \sim \frac{1}{\sqrt{\phi_{\text{star}} R_{\text{arm}}^3}} \sim \frac{1}{\sqrt{\phi_{\text{star}} M_{\text{arm}}^{1.5}}}$$

with  $R_{\text{arm}}$  being the radius of gyration of the star arm, leading one to anticipate a factor of 9.4 difference between the value of  $\chi_e$  for the current blend and that for the blend of Greenberg et al.<sup>5,6</sup> (for which  $\phi = 0.18$ ). The direction of the difference is anticipated by the theory, but the magnitude of the difference is less than expected. The values of  $\chi$  and segment length for the two blends with different sorts of stars considered in the present work are the same within the uncertainty of the analysis, as expected from the similarity of the raw data curves. The slopes of the two curves in Figure 4a are seen to be identical, so if there is an enthalpic contribution to  $\chi$  due to the butadiene units in the star with end-capping, it is not resolvable with SANS. The apparent absence of an enthalpic effect could be due both to the very small number of BD units involved and also to the fact that the BD units lie very close to the cores and therefore may be screened from interactions with styrene units in the linear chain. The values of  $a$

derived from the data (e.g., 6.8 Å for 4PS, 6.9 Å for 4PSwBD at 180 °C) are in good agreement with published values for linear PS (e.g., 6.7 Å at 180 °C from refs 31 and 32). The difference between the values of  $a$  for 4PSwBD and 4PS at any given temperature is always within the experimental uncertainty.

## Conclusion

Two precisely matching 16K 4-arm star polystyrenes, one made with BD end-capping of the arms and one not, were synthesized to probe the impact of the end-capping on various physical properties. MALDI-TOF mass spectral analysis of the arm polymer after BD end-capping proved that the crossover reaction was effective and that no polystyrene without BD units existed in the sample even when the arms were minimally end-capped with only an average of 1.4 equiv of BD. Both the intrinsic viscosities and glass transition temperatures of the two 4-arm star polystyrenes are distinct. In fact, the BD end-capping affects the dynamics profoundly, apparently dynamically decoupling the arms from the core. However, the end-capping does not perturb the bulk thermodynamic interactions in a star/linear blend enough to be unambiguously observed by SANS. This suggests that the careful use of end-capping to create “well-defined” star homopolymers for thermodynamic studies of bulk star/linear blends is not problematic for stars of low functionality but must be accounted for carefully in studies of the effect of architecture on dynamics.

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